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[54] Invention title

The Ag catalyst for ethylene oxide production and its preparative method as well as its application

[57] Abstract

The invention relates to a kind of Ag catalyst for ethylene oxide production by ethylene oxidation; the catalyst is made through the following steps: the solution with compound containing Ag, organic amine, alkali metal assistant, Ce assistant, optio alkali-earth metal assistant, optio Re assistant and its co-assitant is soaked and calcinated into porous α -aluminium oxide carrier, after sieving and drying, and it is activated by mixed gases containing oxygen, then the Ag catalyst is prepared. The Ag catalyst is prepared by this way with high activity and selectivity. The invention also refers to the usage of the stated catalyst in ethylene oxide production by ethylene oxidation.

1. A kind of Ag catalyst used for ethylene oxide production by ethylene oxidation, which is prepared through the following steps:
 - 1) The solution with compound containing Ag, organic amine, alkali metal assistant, Ce assistant, optio alkali-earth metal assistant, optio Re assistant and its co-assitant is used to soak porous α -aluminium oxide carrier.
 - 2) After sieving the maceration extract, the soaked carrier is dried.
 - 3) The carrier got from step two is activated in mixed gas containing oxygen, and the Ag catalyst is made.
2. The Ag catalyst is the same as stated in Claim 1, of the total the porous α -aluminium oxide carrier has the following features: α -aluminium oxide content $\geq 90\%$, optimization $\geq 95\%$, alkali-earth metal content (counted as metal) $\leq 2.0\%$, optimization $\leq 0.8\%$, specific surface is $0.2\sim 2.0\text{ m}^2/\text{g}$, optimization is $0.3\sim 1.5\text{ m}^2/\text{g}$, hole volume is $0.35\sim 0.85\text{ ml/g}$, optimization is $0.4\sim 0.7\text{ ml/g}$, absorption rate $\geq 30\%$, optimization $\geq 40\%$, crushing strength is $20\text{N/piece}\sim 150\text{N/piece}$, optimization is $30\text{N/piece} \sim 120\text{N/piece}$.
3. The Ag catalyst is the same as stated in Claim 1, of the total the Ag compounds are silver oxide, argent nitrate or silver oxalate.
4. The Ag catalyst is the same as stated in Claim 1, of the total the Ag compounds addition should keep the Ag content of $1\%\sim 30\%$ in the stated Ag catalyst, the optimization is $5\%\sim 25\%$, based on the total weight of the stated Ag catalyst.
5. The Ag catalyst is the same as stated in Claim 1, of the total the stated alkali metal assistants are: Li, Na, Ka, Rb or Cs compounds or the combination of any two compounds.
6. The Ag catalyst is the same as stated in Claim 5, of the total the alkali metal is Cs.
7. The Ag catalyst is the same as stated in Claim 5, of the total the alkali metal addition should keep the alkali metal content of $5\text{ppm}\sim 2000\text{oom}$ in the stated Ag catalyst, of the total the optimization is $10\text{ppm}\sim 1200\text{ppm}$, based on the total weight of the stated Ag catalyst.
8. The Ag catalyst is the same as stated in Claim 1, of the total the alkali-earth metal assistants are: Mg, Ca, Al or Ba oxides, carbonite, sulfate, acetate or nitrate, or their mixtures.
9. The Ag catalyst is the same as stated in Claim 8, of the total the alkali-earth metal is Ca.
10. The Ag catalyst is the same as stated in Claim 8, of the total the alkali-earth metal is Ba.
11. The Ag catalyst is the same as stated in Claim 8, of the total the alkali-earth metal is Sr.

12. The Ag catalyst is the same as stated in Claim 8, the stated alkali-earth metal addition should keep the stated alkali-earth metal content of 0ppm~22000ppm in the stated Ag catalyst, of the total the optimization is 0ppm~10000ppm, based on the total weight of the Ag catalyst.
13. The Ag catalyst is the same as stated in Claim 1, of the total the Ce assistant is Ce oxide, carbonite, sulfate, acetate or nitrate, or their mixtures.
14. The Ag catalyst is the same as stated in Claim 13, of the total the Ce addition should keep the content of 1ppm~495ppm in the stated Ag catalyst, the optimization is 5ppm~200ppm, based on the total weight of the stated Ag catalyst.
15. The Ag catalyst is the same as stated in Claim 1, of the total the Reassitants are ReO₃, perrhenic acid or perrhenate, or their mixtures.
16. The Ag catalyst is the same as stated in Claim 15, of the total the Re assistant addition should keep the content of 0ppm~1000ppm in the stated Ag catalyst, the optimization is 0ppm~400ppm, based on the total weight of the stated Ag catalyst.
17. The Ag catalyst is the same as stated in Claim 1, of the total the co-assistant for Re assistant can be compounds of any transition metal, or the mixtures of several transition metal compounds.
18. The Ag catalyst is the same as stated in Claim 17, of the total the co-assistant for Re assistant can be oxacid of VIB and VIIB groups' elements or their salts.
19. The Ag catalyst is the same as stated in Claim 17, of the total the addition of co-assistant for Re assistant should keep the content of 0ppm~500ppm in the stated Ag catalyst, the optimization is 0ppm~300ppm, based on the total weight of the stated Ag catalyst.
20. The Ag catalyst is the same as stated in Claim 1, of the total the stated assistant before soaking Ag, during soaking Ag or after soaking, is exerted on the carrier, or after soaked carrier activated the carrier is soaked.
21. The Ag catalyst is the same as stated in Claim 1, of the total the stated activated process is done in the nitrogen oxygen atmosphere with no more than 21% air or oxygen.
22. The Ag catalyst is the same as stated in Claim 1, of the total the temperature of the stated activated process is controlled between 150°C and 700°C, the optimization is 200°C ~ 500°C.
23. The Ag catalyst is the same as stated in Claim 1, of the total the duration of the stated activated process is 0.5~120 minutes, the optimization is 1~60minutes.

24. A method for the production of ethylene oxide through the oxidation of ethylene, in which the stated Ag catalyst in any item of Claim 1 to 23 is used.

The Ag catalyst for ethylene oxide production, its preparative method and its application

Technology Field

The invention refers to a kind of Ag catalyst and its preparative method, specifically speaking, the invention refers to a kind of Ag catalyst for ethylene oxide production by ethylene oxidation and its preparative method, and also refers to the usage of the catalyst in ethylene oxide production by ethylene oxidation.

Background Technology

By the Ag catalyst, the main product of ethylene oxidation is ethylene oxide, at the same time carbon dioxide and water are produced in side reaction, the activity, selectivity and stability are the main performance indexes. The so called activity means the reaction temperature for the ethylene oxide production progress reaching certain reaction load. The lower the reaction temperature is, the higher the catalyst activity is. The so called selectivity means the r mole ratio of ethylene-into- ethylene oxide and ethylene. The so called stability means that when the activity and selectivity declines with the times goes by, the lower the declining rate is, the higher the stability of the catalyst is. In the ethylene oxide production by ethylene oxide, the usage of Ag catalyst with high activity, selectivity and stability can improve the economic returns, so preparing Ag catalyst with high activity, selectivity and good stability is the main direction for Ag catalyst research. The performance of Ag catalyst is not only related with the ingredients and its preparative method, but also with the performance of the catalyst carrier and its preparative method.

In the present Ag catalyst preparative methods, the two processes, that is, preparation of porous carrier (aluminium oxide) and exerting active ingredient and assistant into the carrier are included.

The main method to make the active ingredient Ag and all kinds of assistants exert on the carrier is the pickling process, that is that the aluminium oxide carrier is soaked into the solution made from silver salt, organic amine and all kinds of assistants, after removing the solution the carrier is heated to reduction to make the soaked carrier active. Alkali metal is the most common assistant; there are few patents which use alkali metals as assistants. US4305844 (corresponding to EP0017725, Huels Chemische Werke AG, 1981) prepared Ag catalyst contains 0.01~0.25% Ba and alkali metal assistant, at beginning, the activity and selectivity are low;

US4350616 (The Dow Chemical Company, 1982) has also used Cs and Ba in the production process of Ag catalyst, but activity of the prepared Ag catalyst is low, the selectivity is not over 84.0%, US4376718 (Huels Chemische Werke AG, 1983) describes that an assistant bed layer is set on the upper part of the reactor, the assistants are from Ka, Rb, Cs and Ba compounds, the stability of the catalyst bed layer is improved; the carrier specific surface for Ag catalyst preparative method given by US4400308 (EC Erdoelchemie GmbH, 1983) is 0.4~0.5 m²/g, the particle diameter of loading Ag is 0.3~0.4 μm, the 0.001~0.03% alkali metal Cs and 0.05~0.5% alkali-earth metal Ba are used, the maximum selectivity of the prepared Ag catalyst is only 81.5%. The patent SU1685510 (Chorine Ind. Res. Des. Int., 1991) used specific surface less than 1m²/g aluminium oxide carrier, the carrier is treated with Ag salt amid comoles compound, alkali metal salt, alkali-earth metals compounds, after drying it is treated by alkali metal salt and surface acting agent, the patent practical alkali-earth metal salts are calcium nitrate and nitrate barium, the effect is not obvious by adding alkali-earth metal, when the time-space yield is less than 180gEO/l/h, the maximum selectivity is 78.2%; DD289413A and DD288067 (Veb Leuna-Werke AG, 1991) has revealed that the acidity solution with organic acid silver, overdose lactic acid, alkali-earth metal and alkali metal is overlaid on the carrier with less than 0.3 m²/g specific surface to make Ag catalyst, the alkali-earth metal is Ba, the selectivity of catalyst is improved, but the maximum selectivity is only 77%; US4812437 (corresponding to EP0247414, Mitsubishi Petrochemical Co., 1989) by using Ag and at least one of Na, Ka, Rb and Cs, they deposit on the carrier containing Al₆Si₂O₁₃, the Na content on the carrier is 0.08~1.2%, the Ba salt is also used in the catalyst preparation, the maximum selectivity of the prepared Ag catalyst is 81.2%; DE3310752 (corresponding to US4760042) and US4841080 (Scientific Design Co., 1988, 1989), the silver is deposited on the carrier with specific surface of 0.3~0.8 m²/g, after activation 50~300ppm alkali metal is deposited, the patent claims that the catalysts include alkali-earth metal assistants and prior Ba, the selectivity of Ag catalyst made in the patent is only 79.7%; WO9613493 (corresponding to EP789693, Shell Int. Research, 1996), the silver, alkali metal assistant, Re assistant and the deposited alkali-earth metal before its assistant, prior Ba and/or Mg are deposited in Ag catalyst with Re preparation, only the catalyst made by deposited alkali-earth metal and Ag as well as alkali metal assistant has relative high selectivity, but the selectivity is only 81.5%, the initial activity of the Ag catalyst with Re is improved by pre-deposited alkali-earth metal in this patent.

In patent WO9713579, the selectivity of catalyst made by cerate, alkali metal, alkali-earth metal and any Re assistant gets to 85.0%.

CN1038411 reveals a Ag catalyst loaded with aluminium oxide, with the composition of $\text{Ag}_a\text{Ba}_b\text{K}_c\text{Cs}_d\text{Na}_e\text{La}_f\text{Ce}_g$, when $a=100$, $b=0.01\sim10$, $c=0.1\sim10$, $d=0.1\sim10$, $e=0.01\sim0.05$, $f=0.5\sim5$, the Ag catalyst selectivity is 83.5% in patent.

Although alkali-earth metal assistant and Ce are used in the above patent documentation, the results are still not satisfactory; as a result, a kind of Ag catalyst and its preparative method with great all-round improvement on activity and selectivity is in great needed in this field.

Invention Content

Given the above present technique conditions, the inventor of the invention has done wide and deep research in the AG catalyst field, the results is discovered that the initial activity and selectivity of Ag catalyst in ethylene oxidizing reaction are both improved, the Ag catalyst is prepared by soaking porous aluminium oxide carrier with the solution of silver compound, organic amine and specified assistant and then the heat-treating in nitrogen oxygen atmosphere with less than 21% air or oxygen. $\alpha\text{-Al}_2\text{O}_3$ carrier with the specific surface between 0.2 and $2.0\text{m}^2/\text{g}$ is selected in the invention, soaking in the solution made from silver salt, organic amine, alkali metal assistant, Ce assistant, arbitrary alkali-earth metal assistant and arbitrary Re assistant as well as co-assistants, after drying and activation the Ag catalyst is prepared with relative high initial performance.

As a result, one aim of the invention is to provide a kind of new Ag catalyst; it displays good initial activity and selectivity in ethylene oxide production by ethylene oxidation.

One aim of the invention is to provide a preparative method of the Ag catalyst stated above.

Another aim of the invention is to provide the application of the Ag catalyst stated above in ethylene oxide production by ethylene oxidation.

These and other aims, features and advantages of the invention can be clearer after reading the specifications.

The details of this invention

The invention provides a kind of new Ag catalyst on one hand; the stated catalyst is prepared through the following steps:

- 1) The porous $\alpha\text{-Al}_2\text{O}_3$ carrier is soaked in the solution made from silver compounds with enough content of Ag, organic amine, alkali metal assistant, Ce assistant, arbitrary alkali-earth metal assistant and arbitrary Re assistant as well as co-assitants;

- 2) After the maceration extract is sieved, the soaked carrier should be dried; and
- 3) The carrier got from the step 2) should be activated in the mixture gas with oxygen and the Ag catalyst is prepared.

On the other hand, this invention relates to the application of the abovementioned new type Ag catalyst in the production of epoxyethane by ethylene oxidation.

The porous α - Al_2O_3 carrier for the Ag catalyst in this invention is the porous α - Al_2O_3 with α - $\text{Al}_2\text{O}_3 \geq 90\%$, the optimization $\geq 95\%$. During the preparation of the carrier, the salt of the alkali-earth metal such as Mg, Ca, Sr and Ba, like sulfate, phosphate and carbonate, sulfate and carbonate is preferred, the BaSO_4 and BaCO_3 are the best. Based on the total weight of the porous α - Al_2O_3 carrier, the alkali metal content is counted not more than 2.0%, the optimization is not more than 0.8%. The crushing strength of the carrier is 20N/piece~150N/piece, the optimization is 30N/piece~120N/piece; the specific surface is 0.2~2.0 m^2/g , the optimization is 0.3~1.5 m^2/g ; absorption rate $\geq 30\%$, the optimization $\geq 40\%$, the hole volume is 0.35~0.85ml/g, the optimization is 0.4~0.7ml/g. Porous α - Al_2O_3 carrier can be any regular carrier form, such as pill shape, globular, annuli form, strip shape, radial porous pillar shape, the annuli form is preferred.

The Ag catalyst of this invention is prepared by drying and calcinating the above Al_2O_3 carrier soaked with the solution made from compounds with Ag content, organic amine, alkali metal assistant, Ce assistant, arbitrary alkali-earth metal assistant and arbitrary Re assistant as well as co-assistants.

The silver compounds used in the invention can be those familiars to the practiced technicians, such as Ag_2O , silver oxalate, AgNO_3 , Ag_2SO_4 , silver carbonate, silver phosphate, the AgNO_3 is preferred. For the invention, the organic amine which can be used are those familiars to the practiced technicians, such as pyridine, ethylamine, N-propylamine, isopropylamine, n-butylamine, sec-butylamine, isobutylamine, tert-butylamine, ethanediamine, 1,3-propanediamine, 1,2-propanediamine, 1,4-tetramethylenediamine, 1,2-tetramethylenediamine, 1,3-tetramethylenediamine, tetramethylenediamine, tetramethylenediamine, butanolamine or their mixture. Prior organic amine are pyridine, butanolamine, ethanediamine, 1,3-propanediamine, cholamine or their mixtures.

The Ag catalyst of this invention, for example, can be prepared as the following method: AgNO_3 solution and ethanedioic acid amine or ethanedioic acid aqueous solution have reaction firstly, silver oxalate sediment educed, after colation, it is washed by deionized water until there is no nitrate ion, then silver oxalate is dissolved into organic amine such as: pyridine, butylamine, ethanediamine, 1,3-propanediamine, cholamine or their mixture water solution, the assistant is added to prepare the dipping solution, then the above aluminium oxide carrier is soaked by the prepared dipping solution, after dropping dry, in the air flow or not more than 21% oxygen content nitrogen oxygen atmosphere, under the temperature of 150 ~ 700°C, the

optimization one is 200~500°C temperature extent, kept for 0.5 minute ~ 120 minutes, the optimization is 1 ~ 60minutes, for the thermolysis.

The Ag_2O can also be replaced by AgNO_3 , silver oxalate can not be educed and sieved, complexation is done directly with organic amine, and then the carrier is soaked. The content of Ag compounds used in the soaking process in the invention is enough to make the final prepared catalyst contain 1~30% weight, the optimization is 5~25% weight, it is counted by the catalyst total weight.

The alkali metal assistant in the invention can be Li, Na, Ka, Rn or Cs compounds or combination of any two kinds, such as Li, Na, Ka, Rn or Cs oxide, hydroxide, muriate, sulfate, nitrate, carbonate, phosphate, the optimization are Cs oxide, hydroxide, muriate, sulfate, nitrate, carbonate, phosphate, the best are cesium sulfate and cesium carbonate. In the final Ag catalyst, alkali metal content based on final catalyst weight is 5~2000ppm, the optimization is 10~1200 ppm. The alkali metal assistant can be loaded to the carrier before, during or after soaking, as well as be soaked in the carrier after the soaked carrier is activated.

The alkali-earth metal assistant in the invention can be Mg, Ca, Sr or Ba compounds, such as oxide, carbonite, sulfate, acetate or nitrate, or its mixture, the optimization is acetate, the more optimized is strontium acetate and barium acetate. In the final Ag catalyst, alkali-earth metal content based on the final catalyst weight is 0~22000ppm, the optimization is 0~10000ppm. Alkali-earth metal assistant can be loaded to the carrier before, during or after soaking, as well as be soaked in the carrier after the soaked carrier is activated.

The Ce assistant in the invention can be Ce oxide, carbonite, sulfate, acetate or nitrate, or their mixture, the optimization is Ce carbonite and acetate, such as acetic Ce and cerium oxalate. In the final Ag catalyst, Ce content based on the final catalyst weight is 1~495ppm, the optimization is 5~200ppm. Ce metal assistant can be loaded to the carrier before, during or after soaking Ag, as well as be soaked in the carrier after the soaked carrier is activated.

The Re assistant can be Re oxide, perrhenic acid, perrhenic acid salt, or their mixtures, the optimization is perrhenic acid, perrhenic acid salt, such as perrhenic acid, perrhenic acid Cs and perrhenic acid amine. In the final Ag catalyst, the Re content based on the final catalyst weight is 0~1000 ppm, the optimization is 0~400 ppm. The Re assistant can be loaded to the carrier before, during or after soaking Ag, as well as be soaked in the carrier after the soaked carrier is activated.

The co-assistant of the Re assistant in the invention can be any transition metal compounds in the periodic chart or mixtur es of several kinds of transition metal compounds, the optimization is VIB and VIIB elements' oxacid and their salts, such as tungstic acid, tungstic Cs, molybdenic acid and molybdenic amine.

In the final Ag catalyst, the content of co-assistant of the Re assistant based on the final catalyst weight is 0~500 ppm, the optimization is 0~300 ppm. The co-assistant of Re assistant can be loaded to carrier before, during or after soaking Ag, and also can be loaded to the carrier after the soaked carrier activated.

The determination of the performance of catalyst

All kinds of Ag catalysts in the invention is detected by laboratory reactor (following a brief microreaction) to evaluate the initial performance and stability of the devices. The reactor for microreaction evaluation device is stainless steel tube with inner diameter of 4mm, and the reactor is put in the heating mantles. The admission space of the catalyst is 1ml, there is inert filler in the bottom to make catalyst bed layer stay in the constant temperature zone.

The determination of its initial activity and selectivity

The conditions used for the determination of its activity and selectivity

The composition of the reactive gases (mol %)

Ethylene (C ₂ H ₄)	28±1
Oxygen (O ₂)	7.4±0.2
Carbon dioxide	< 8
Stable gas (N ₂)	allowance
Catastaltic dichlorethane	0.1 ppm ~ 2.0 ppm
Reaction pressure	2.1 MPa
Air speed	7000/h
EO density from the reactor outlet	1.35%
Time-space yield	185gEO/mlCat./h

When the reaction reaches stable, the gas composition of the reactor inlet and outlet is continuously detected. The detecting results are corrected by volume construction, and then the selectivity is counted according to the following formula:

$$\text{Selectivity } S = \frac{\Delta \text{EO}}{\Delta \text{EO} + 0.5 \cdot \Delta \text{CO}_2} \times 100\%$$

ΔEO is the ethylene oxide density difference between outlet gases and inlet gases, ΔCO_2 is the CO₂ density difference between outlet gases and inlet gases, select the average of over 10 group experiment data as the trial result.

Compared with the present techniques, this invention has the following advantages: porous aluminium oxide carrier is used in the preparation of Ag catalyst according to the invention and added with little Ce metal assistant, the prepared catalyst has relative high activity and selectivity, the catalyst is especially fit for reaction for ethylene oxide production by ethylene oxidation.

Example

The invention is further specified with the following examples, but the extent of the invention is not limited in the examples.

Carrier 1 and 2:

312g α - Al_2O_3 trihydrate of 30~500 mesh, 104g Al_2O_3 hydrate of 30~200 mesh, 81g oil coke, 7g NH_4F , 8.5g $\text{Mg}(\text{NO}_3)_2$ and BaSO_4 (0g and 1.2g respectively) are put into blender to misce bene, and then transferred to kneading machine, 0.18L thin nitric acid (nitric acid: water=1:3, proportion by weight) is added, the shaping cream is kneaded and extruded. The extrusion shape is wreath with 8.0mm outer diameter, 6.0mm length and 2.0mm inner diameter, under the temperature of 80 ~ 120°C, it is dried more two hours so that the liberation water content declines below 10%.

The above two wreaths are put into the bell jar kiln, after 30 hours, the temperature goes up from the room temperature to 1350°C ~ 1550°C, the temperature should be kept for two hours, then white α - Al_2O_3 carrier sample 1 and carrier sample 2 are obtained.

Carrier 3:

312g α - Al_2O_3 trihydrate of 30~500 mesh, 104g Al_2O_3 hydrate of 30~200 mesh, 81g oil coke, 7g NH_4F , 8.5g $\text{Mg}(\text{NO}_3)_2$ are put into blender to misce bene, and then transferred to kneading machine, 0.15L thin nitric acid (nitric acid: water=1:3, proportion by weight) is added, the shaping cream is kneaded and extruded. The extrusion shape is wreath with 8.0mm outer diameter, 6.0mm length and 2.0mm inner diameter, under the temperature of 80 ~ 120°C, it is dried more two hours so that the liberation water content declines below 10%.

The above wreath is put into the bell jar kiln, after 30 hours, the temperature goes up from the room temperature to 1350°C ~ 1550°C, the temperature should be kept for two hours, then white α - Al_2O_3 carrier sample 3 is got.

After detecting, the composition and physical property of the carrier can refer to table 1.

Table 1 Physical property data of Carrier 1~3

	Carrier 1	Carrier 2	Carrier 3
α - Al_2O_3 content	98.2	97.8	98.4
BaO content	0	0.35	0
Crushing Strength (N/P)	52	47	86
Absorption Rate (%)	61	64	47

Bulk specific density (g/cm ³)	0.54	0.52	0.64
Specific Surface (m ² /g)	0.87	0.98	0.91
Hole Volume (ml/g)	0.68	0.65	0.58
Distribution of the pore radius (percent of total pore volume %)			
<0.5μm	20.5	19.8	17.0
0.5~1μm	4.1	4.9	4.5
1~5μm	51.4	53.5	63.7
5~10μm	10.7	9.8	9.6
10~30μm	9.2	9.6	3.4
30~51μm	1.5	1.5	0.9
>51μm	1.6	0.9	0.9

The preparation of the catalyst:

Comparative examples 1-3:

700g AgNO₃ is dissolved in 750ml deionized water to make AgNO₃ solution. 325g ethanedioic amine is dissolved in 250ml 50°C deionized water to make ethanedioic amine solution. The two solutions are mixed to form white silver oxalate sediment under severely stirring. Aging more than 30 minutes, sieved, the sediment is washed by deionized water till there is no NO₃⁺. Filter cake contains about 60% Ag, and 15% water, it is cream.

300g ethanediamine, 110g cholamine, 375g deionized water are added in the glass container with stirrer. Silver oxalate cream got from the upper face by stirring is slowly added into the mixing solution, the temperature is kept under 40°C to make the silver oxalate dissolve entirely, the addition of silver oxalate makes the produced maceration extract contain 22% Ag (weight). 2.2g cesium sulfate, 1.1g barium acetate and deionized water are added to make the solution total weight reach 2000g for the future usage.

100g carrier sample 1, 2, 3 are put into container which can be drawn vacuum respectively. Drawn vacuum to 10mmHg above, the above maceration extract is put in; the carrier is immersed and kept for 30 minutes.

The redundant solution is sieved. The soaked carrier is heated for 5 minutes in 400°C air flow, cooling down, then ethylene oxide Ag catalyst comparative example 1, 2 and 3 are prepared.

Examples 1-9:

Repeat the same procedure of Comparative examples 1-3, the different is that the maceration extract contains other cerous sulfate; the dosage is shown in the following table 2.

Table 2 the addition of Ce assistant in the preparative process for examples 1-9 catalyst sample.

Example No.	Carrier No.	Addition of cerous sulfate
Example One	1	0.09
Example Two	1	0.17
Example Three	2	0.35
Example Four	2	0.09
Example Five	2	0.17
Example Six	2	0.35
Example Seven	3	0.09
Example Eight	3	0,17
Example Nine	3	0.35

The contents of Ag and assistant in the prepared catalyst are analyzed, and the results are listed in table 3, and the content is counted to metal.

The micro reaction evaluation device is used to detect the activity and selectivity of the catalyst sample in the craft condition stated above, the trial results are listed in the following table 3.

Table 3 The trial results of the catalyst samples in examples 1-9

Example No.	Ag content (%)	Cs content (ppm)	Ce content (ppm)	Reaction temperature (°C)	EO(%)	Selectivity (%)
Comparative example 1	16.5	639	0	226.5	1.36	83.1
Example 1	17.0	642	15	221.8	1.36	83.7
Example 2	16.8	638	41	220.5	1.35	83.9
Example 3	17.1	635	103	223.6	1.37	83.6
Comparative example 2	16.9	642	0	224.8	1.35	83.3
Example 4	17.2	645	16	221.0	1.36	83.9
Example 5	16.6	634	43	220.4	1.36	84.3
Example 6	17.1	640	112	222.0	1.34	83.7
Comparative example 3	14.6	554	0	220.7	1.35	82.9
Example 7	17.2	668	11	217.4	1.38	83.5
Example 8	17.2	666	36	215.6	1.36	83.7
Example 9	17.3	662	87	216.8	1.35	83.6

Comparative example 4

300g ethanediamine, 110g cholamine and 375g deionized water are added into the glass container with a stirrer. Silver oxalate cream produced in the stated Comparative example 1-3 by stirring is slowly added into the mixing solution, the temperature is kept under 40°C to make the silver oxalate dissolve entirely, the addition of silver oxalate makes the produced maceration extract contain 22% Ag (weight). 2.2g cesium sulfate, 1.1g strontium acetate and deionized water are added to make the solution total weight reach 2000g for the future usage.

100g carrier sample 2 is put into container which can be drawn vacuum respectively. Drawn vacuum to 10mmHg above, the above maceration extract is put in; the carrier is immersed and kept for 30 minutes. The redundant solution is sieved. The soaked carrier is heated for 5minutes in 400°C air flow, cooling down, then ethylene oxide Ag catalyst Comparative example 4 is prepared.

Example 10-12

Repeat the same procedure of Comparative example 4, the different is that the maceration extract contains other cerium acetate or cerium oxalate; the dosage is shown in the following table 4.

Table 4 The addition of Ce assistant in example 10-12 catalyst sample preparation process

Example No.	Ce assistant category	Addition (g)
Example 10	cerium acetate	0.19
Example 11	cerium acetate	0.38
Example 12	cerium oxalate	0.15

The content of Ag and assistant in the prepared catalyst is analyzed, and the results are listed in table 5, in which the content is counted as metal.

Micro reaction evaluation device is used to detect the activity and selectivity of catalyst sample in the craft condition stated above, the trial results are listed in the following table 5.

Table 5 The trial results of the catalyst samples in example 10-12

Example No.	Ag content (%)	Cs content (ppm)	Ce content (ppm)	Reaction temperature (°C)	EO (%)	Selectivity (%)
Comparative example 4	16.5	639	0	224.7	1.36	83.3
Example 10	17.0	642	43	220.8	1.36	83.7
Example 11	16.8	638	98	219.3	1.35	84.3
Example 12	17.1	635	47	221.6	1.7	83.8

Comparative example 5

300g ethanediamine, 110g cholamine and 375g deionized water are added in the glass container with stirrer. Silver oxalate cream produced in the stated Comparative example 1-3 by stirring is slowly added into the mixing solution,

the temperature is kept under 40°C to make the silver oxalate dissolve entirely, the addition of silver oxalate makes the produced maceration extract contain 22% Ag (weight). 2.2g cesium sulfate and deionized water are added to make the solution total weight reach 2000g for the future usage.

100g carrier sample 2 is put into container which can be drawn vacuum respectively. Drawn vacuum to 10mmHg above, the above maceration extract is put in; the carrier is immersed and kept for 30 minutes. The redundant solution is sieved. The soaked carrier is heated for 5minutes in 300°C air flow, cooling down, then ethylene oxide Ag catalyst Comparative example 5 is prepared.

Example 13-14

Repeat the same procedure of Comparative example 5, the different is that the maceration extract contains 0.35g and 3.8g cerous sulfate.

The Ag and assistant content of the prepared catalyst is analyzed, the results are listed in table 6, and the content is counted to metal.

The micro reaction evaluation device is used to detect the activity and selectivity of the catalyst sample in the craft condition stated above, the results are listed in the following table 6.

Comparative example 6

Repeat the same procedure of Comparative example 5, the different is that the maceration extract contains 5.0g cerous sulfate.

The Ag and assistant content of the prepared catalyst is analyzed, the results are listed in table 6, and the content is counted to metal.

The micro reaction evaluation device is used to detect the activity and selectivity of the catalyst sample in the craft condition stated above, the results are listed in the following table 6.

Table 6 the trial results of the catalyst sample in Example 13

Example No.	Ag content (%)	Cs content (ppm)	Ce content (ppm)	Reaction temperature (°C)	EO (%)	Selectivity (%)
Comparative example 5	16.5	639	0	223.7	1.36	82.7
Example 13	17.0	642	43	217.3	1.34	83.5
Example 14	16.8	633	452	221.9	1.35	83.0
Example 6	16.1	612	623	227.0	1.35	82.6

Comparative example 7

300g ethanediamine, 110g cholamine, 375g deionized water are added in the glass container with stirrer. Silver oxalate cream produced in the stated Comparative example 1-3 by stirring is slowly added into the mixing solution, the temperature is kept under 40°C to make the silver oxalate dissolve entirely, the addition of silver oxalate makes the produced maceration extract contain 22% Ag (weight). 2.0g cesium sulfate, 0.6g perhenic acid, 0.1g ammonium molybdate and deionized water are added to make the solution total weight reach 2000g for the future usage.

100g carrier sample 2 is put into container which can be drawn vacuum respectively. Drawn vacuum to 10mmHg above, the above maceration extract is put in; the carrier is immersed and kept for 30 minutes. The redundant solution is sieved. The soaked carrier is heated for 5minutes in 230°C air flow, cooling down, then ethylene oxide Ag catalyst Comparative example 7 is prepared.

Example 15

Repeat the same procedure of Comparative example 5, the different is that the maceration extract contains 0.35g cerous sulfate.

The Ag and assistant content of the prepared catalyst is analyzed, the results are listed in table 6, and the content is counted to metal.

The micro reaction evaluation device is used to detect the activity and selectivity of the catalyst sample in the craft condition stated above, the results are listed in the following table 6.

Table 6 The trial results of the catalyst sample in Example 15

Example No.	Ag content (%)	Cs content (ppm)	Ce content (ppm)	Re content (ppm)	Mo content (ppm)	Reaction temperature (°C)	EO (%)	Selectivity (%)
Comparative example 7	16.5	639	0	205	32	227.4	1.36	83.9
Example 15	17.0	642	43	210	35	222.6	1.34	84.7

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权利要求书 3 页 说明书 12 页

[54] 发明名称

用于生产环氧乙烷的银催化剂、其制备方法及其应用

[57] 摘要

本发明涉及一种用于乙烯氧化生产环氧乙烷的银催化剂，该催化剂通过如下方法得到：用含银化合物、有机胺、碱金属助剂、铈助剂、任选的碱土金属助剂和任选的铈助剂及其共助剂的溶液浸渍经高温焙烧制成的多孔 α -氧化铝载体，沥滤干燥后，用含氧混合气活化，制成银催化剂。用这种方法制造的银催化剂具有较高的活性和选择性。本发明还涉及所述催化剂在乙烯氧化生产环氧乙烷中的用途。

1. 一种由乙烯氧化生产环氧乙烷所用的银催化剂，通过包括以下步骤的方法制备：

- 1) 用含足够量的银化合物、有机胺、碱金属助剂、铈助剂、任选的碱土金属助剂和任选的镧助剂及其共助剂的溶液浸渍多孔 α -氧化铝载体；
- 2) 滤去浸渍液后，干燥浸渍过的载体；和
- 3) 在含氧混合气体中对步骤2)所得载体进行活化，制成所述银催化剂。

2. 如权利要求1所述的银催化剂，其中多孔 α -氧化铝载体具有以下特征： α -氧化铝含量 $\geq 90\%$ ，优选 $\geq 95\%$ ，碱土金属含量(以金属计) $\leq 2.0\%$ ，优选 $\leq 0.8\%$ ，比表面为 $0.2 \sim 2.0\text{m}^2/\text{g}$ ，优选 $0.3 \sim 1.5\text{m}^2/\text{g}$ ，孔容为 $0.35 \sim 0.85\text{ml/g}$ ，优选 $0.4 \sim 0.7\text{ml/g}$ ，吸水率 $\geq 30\%$ ，优选 $\geq 40\%$ ，压碎强度为 $20\text{N/粒} \sim 150\text{N/粒}$ ，优选 $30\text{N/粒} \sim 120\text{N/粒}$ 。

3. 如权利要求1所述的银催化剂，其中银化合物为氧化银、硝酸银或草酸银。

4. 如权利要求1所述的银催化剂，其中银化合物的加入量应使银在所述银催化剂中的含量为 $1\% \sim 30\%$ ，优选 $5\% \sim 25\%$ ，基于所述银催化剂的总重量。

5. 如权利要求1所述的银催化剂，其中所述碱金属助剂为锂、钠、钾、铷或铯的化合物或其任意两种的组合。

6. 如权利要求5所述的银催化剂，其中所述碱金属为铯。

7. 如权利要求5所述的银催化剂，其中所述碱金属的加入量应使所述碱金属在所述银催化剂中的含量为 $5\text{ppm} \sim 2000\text{ppm}$ ，优选 $10\text{ppm} \sim 1200\text{ppm}$ ，基于所述银催化剂的总重量。

8. 如权利要求1所述的银催化剂，其中所述碱土金属助剂为镁、钙、锶或钡的氧化物、草酸盐、硫酸盐、醋酸盐或硝酸盐，或其混合物。

9. 如权利要求8所述的银催化剂，其中所述碱土金属为钙。

10. 如权利要求8所述的银催化剂，其中所述碱土金属为钡。

11. 如权利要求8所述的银催化剂，其中所述碱土金属为锶。

12. 如权利要求 8 所述的银催化剂, 其中所述碱土金属的加入量应使所述碱土金属在所述银催化剂中的含量为 0ppm ~ 22000ppm, 优选 0ppm ~ 10000ppm, 基于所述银催化剂的总重量。

13. 如权利要求 1 所述的银催化剂, 其中所述铈助剂为铈的氧化物、草酸盐、硫酸盐、醋酸盐或硝酸盐, 或其混合物。

14. 如权利要求 13 所述的银催化剂, 其中所述铈助剂的加入量应使在所述银催化剂中的含量为 1ppm ~ 495ppm, 优选 5ppm ~ 200ppm, 基于所述银催化剂的总重量。

15. 如权利要求 1 所述的银催化剂, 其中所述铈助剂为氧化铈、高铈酸或高铈酸盐, 或其混合物。

16. 如权利要求 15 所述的银催化剂, 其中所述铈助剂的加入量应使在所述银催化剂中的含量为 0ppm ~ 1000ppm, 优选 0ppm ~ 400ppm, 基于所述银催化剂的总重量。

17. 如权利要求 1 所述的银催化剂, 其中所述铈助剂的共助剂为元素周期表中任一过渡金属的化合物, 或几种过渡金属化合物的混合物。

18. 如权利要求 17 所述的银催化剂, 其中所述铈助剂的共助剂为 VIB 族和 VIIB 族元素的含氧酸及其盐。

19. 如权利要求 17 所述的银催化剂, 其中所述铈助剂的共助剂的加入量应使在所述银催化剂中的含量为 0ppm ~ 500ppm, 优选 0ppm ~ 300ppm, 基于所述银催化剂的总重量。

20. 如权利要求 1 所述的银催化剂, 其中所述助剂在浸渍银之前、同时或之后施加到载体上, 或在浸渍过的载体活化以后浸渍在载体上。

21. 如权利要求 1 所述的银催化剂, 其中所述活化过程是在空气或氧含量不大于 21% 的氮氧混合气中进行的。

22. 如权利要求 1 所述的银催化剂, 其中所述活化过程的温度控制在 150°C ~ 700°C 之间, 优选 200°C ~ 500°C。

23. 如权利要求 1 所述的银催化剂, 其中所述活化过程的时间是 0.5 分钟 ~ 120 分钟, 优选 1 分钟 ~ 60 分钟。

24. 一种由乙烯氧化生产环氧乙烷的方法, 其中使用如权利要求 1 ~

23 中任一项所述的银催化剂。

用于生产环氧乙烷的银催化剂、其制备方法及其应用

技术领域

本发明涉及一种银催化剂及其制备方法，更具体地说本发明涉及一种用于由乙烯氧化生产环氧乙烷的银催化剂及其制备方法，还涉及这种催化剂在乙烯氧化生产环氧乙烷中的用途。

背景技术

在银催化剂作用下乙烯氧化主要生成环氧乙烷，同时发生副反应生成二氧化碳和水，其中活性、选择性和稳定性是银催化剂的主要性能指标。所谓活性是指环氧乙烷生产过程达到一定反应负荷时所需的反应温度。反应温度越低，催化剂的活性越高。所谓选择性是指反应中乙烯转化成环氧乙烷的摩尔数和乙烯的总反应摩尔数之比。所谓稳定性则表示为活性和选择性随时间的下降速率，下降速率越小，催化剂的稳定性越好。在乙烯氧化生产环氧乙烷的过程中使用高活性、高选择性和稳定性良好的银催化剂可以大大提高经济效益，因此制造高活性、高选择性和良好稳定性的银催化剂是银催化剂研究的主要方向。银催化剂的性能除和催化剂的组成及制备方法有重要关系外，还与催化剂使用的载体的性能和制备方法有重要关系。

现有技术中银催化剂的制备方法包括多孔载体(如氧化铝)的制备和施加活性组分以及助剂到所述载体上这两个过程。

把活性组分银及各种助剂施加到载体上的方法主要是浸渍法，即把氧化铝载体浸于银盐、有机胺以及各种助剂制成的溶液中，除去溶液后加热还原使浸渍后的载体活化。碱金属是最常用的助剂，使用碱土金属助剂的专利不多。US4305844(对应于 EP0017725, Huels Chemische Werke AG, 1981)制成的银催化剂含钡 0.01-0.25%和碱金属助剂，初始活性和选择性都很低；US4350616(The Dow Chemical Company, 1982)

也在银催化剂制造过程中使用了铯和钡,但制成的银催化剂的活性都很低,选择性不超过 84.0%;US4376718(Huels Chemische Werke AG, 1983)描述了在反应器的上段设置助剂床层,助剂选自钾、铷、铯、钡的化合物,提高了催化剂床层的稳定性;US4400308(EC Erdoelchemie GmbH, 1983)披露的银催化剂制备方法使用的载体比表面为 $0.4-0.5\text{m}^2/\text{g}$,负载银的粒径为 $0.3-0.4\mu\text{m}$,使用 0.001-0.03%的碱金属铯和 0.05-0.5%的碱土金属钡,制成的银催化剂选择性最高仅达 81.5%;SU1685510(Chlorine Ind. Res. Des. Int., 1991)使用比表面小于 $1\text{m}^2/\text{g}$ 的氧化铝载体,用银盐的胺基络合物、碱金属盐、碱土金属化合物处理载体,干燥后再用碱金属盐和表面活性剂处理,专利使用的碱土金属盐是硝酸钙和硝酸钡,加入碱土金属取得的效果不明显,时空产率小于 180gEO/l/h 时选择性最高为 78.2%;DD289413A 和 DD288067(Veb Leuna-Werke AG, 1991)披露了用有机酸银、过量乳酸、碱土金属和碱金属的酸性溶液涂到比表面小于 $0.3\text{m}^2/\text{g}$ 的载体上制备银催化剂的方法,使用的碱土金属为钡,使催化剂选择性有所改善,但最高选择性仅为 77%;US4812437(对应于 EP0247414, Mitsubishi Petrochemical Co., 1989)用银和选自钠、钾、铷、铯的至少一种,沉积在含 $\text{Al}_6\text{Si}_2\text{O}_{13}$ 的载体上,载体上钠含量高达 0.08-1.2%,在催化剂制备过程中也使用了钡盐,制成的银催化剂的选择性最高达到 81.2%;DE3310752(对应于 US4760042)和 US4841080(Scientific Design Co., 1988, 1989)先沉积银在比表面为 $0.3-0.8\text{m}^2/\text{g}$ 的载体上,活化后再沉积碱金属 50-300ppm,专利声称催化剂也包括碱土金属助剂,优选钡,该专利制成的银催化剂的选择性仅达到 79.7%;WO9613493(对应于 EP789693, Shell Int. Research, 1996)在制备含铈银催化剂时沉积银、碱金属助剂、铈助剂及其协助剂之前先沉积碱土金属,优选钡和/或镁,专利中仅沉积碱土金属和银及碱金属助剂制成的催化剂的初活性较高,但选择性仅达到 81.5%,该专利通过预沉积碱土金属改善含铈银催化剂的初活性。

WO9713579 将铈盐与碱金属、碱土金属和任选的铈助剂一起使用制成的催化剂选择性达到 85.0%;CN1038411 披露了组成为

$\text{Ag}_a\text{Ba}_b\text{K}_c\text{Cs}_d\text{Na}_e\text{La}_f\text{Ce}_g$ 的负载氧化铝银催化剂, 其中 $a=100$ 时, $b=0.01 \sim 10$, $c=0.1 \sim 10$, $d=0.1 \sim 10$, $e=0.01 \sim 0.05$, $f=0.5 \sim 5$, $g=0.5 \sim 5$, 专利发明的银催化剂选择性可达 83.5%。

尽管上述专利文献使用了碱土金属助剂和 Ce, 但取得的效果仍难以令人满意, 因此本领域仍然需要一种在活性和选择性上全面得到改进的银催化剂及其制备方法。

发明内容

鉴于上述现有技术的状况, 本发明的发明人在银催化剂领域进行了广泛深入的研究, 结果发现将多孔氧化铝载体用由银化合物、有机胺和特定的助剂配制成的溶液浸渍, 经在空气或氧含量小于 21% 的氮氧混合气中热处理后所制备的银催化剂在乙烯氧化反应中的初始活性和初始选择性均得到了改善。本发明使用比表面在 $0.2\text{--}2.0\text{m}^2/\text{g}$ 之间的 $\alpha\text{-Al}_2\text{O}_3$ 载体, 浸渍在银盐、有机胺、碱金属助剂、铈助剂、任选的碱土金属助剂和任选的镱助剂及其共助剂组成的混合溶液中, 经干燥活化后制成银催化剂, 具有较高的初始性能。

因此, 本发明的一个目的是提供一种新型银催化剂, 其在乙烯氧化生产环氧乙烷的过程中显示出良好的初始活性和初始选择性。

本发明的另一目的是提供一种上述银催化剂的制备方法。

本发明的再一目的是提供上述银催化剂在乙烯氧化生产环氧乙烷中的应用。

本发明的这些和其他目的、特征以及优点在阅读完本说明书后将变得更加明了。

发明详述

本发明一方面提供了一种新型银催化剂, 所述催化剂通过包括如下步骤的方法制备:

1) 用含足够量的银化合物、有机胺、碱金属助剂、铈助剂、任选的碱土金属助剂和任选的镱助剂及其共助剂的溶液浸渍多孔 α -氧化铝载体;

- 2) 滤去浸渍液后, 干燥浸渍过的载体; 和
- 3) 在含氧混合气体中对步骤 2) 所得载体进行活化, 制成所述银催化剂。

本发明另一方面涉及上述新型银催化剂在乙烯氧化生产环氧乙烷中的应用。

用于本发明银催化剂中的多孔 α - Al_2O_3 载体是 α - Al_2O_3 含量 $\geq 90\%$, 优选 $\geq 95\%$ 的多孔 α - Al_2O_3 载体。在制备该载体时可加入碱土金属如镁、钙、锶和钡的盐, 如硫酸盐、磷酸盐、碳酸盐等, 优选硫酸盐和碳酸盐, 更优选硫酸钡和碳酸钡。基于多孔 α - Al_2O_3 载体的总重量, 碱土金属的含量以金属计 $\leq 2.0\%$, 优选 $\leq 0.8\%$ 。这种载体的压碎强度为 20N/粒 ~ 150N/粒, 优选 30N/粒 ~ 120N/粒; 比表面为 $0.2 \sim 2.0 \text{ m}^2/\text{g}$, 优选 $0.3 \sim 1.5 \text{ m}^2/\text{g}$; 吸水率 $\geq 30\%$, 优选 $\geq 40\%$; 孔容为 $0.35 \sim 0.85 \text{ ml/g}$, 优选 $0.4 \sim 0.7 \text{ ml/g}$ 。多孔 α - Al_2O_3 载体可呈任何常规载体形式, 例如粒状、球形、环形、条形、径向多孔柱状等, 优选环形。

本发明的银催化剂通过用一种含银化合物、有机胺、碱金属助剂、铈助剂、任选的碱土金属助剂和任选的铈助剂及其共助剂的溶液浸渍上述氧化铝载体并随后干燥和煅烧来制备。

本发明中使用的银化合物可以是本领域熟练技术人员熟知的那些, 例如氧化银、草酸银、硝酸银、硫酸银、碳酸银和磷酸银, 优选硝酸银。对本发明而言, 可以使用的有机胺是本领域熟练技术人员熟知的那些, 例如吡啶、乙胺、正丙胺、异丙胺、正丁基胺、仲丁基胺、异丁基胺、叔丁基胺、乙二胺、1,3-丙二胺、1,2-丙二胺、1,4-丁二胺、1,2-丁二胺、1,3-丁二胺、乙醇胺、丙醇胺、丁醇胺, 或者它们的混合物。有机胺优选是吡啶、丁胺、乙二胺、1,3-丙二胺、乙醇胺或其混合物。

本发明银催化剂例如可以按如下方式制备: 首先使硝酸银的水溶液与草酸铵或草酸水溶液反应, 析出草酸银沉淀, 过滤后, 用去离子水洗涤, 直至无硝酸根离子, 然后把草酸银溶入有机胺如吡啶、丁胺、乙二胺、1,3-丙二胺、乙醇胺或其混合物的水溶液中, 加入助剂, 配成浸渍溶液。然后用所得浸渍溶液浸渍上述氧化铝载体, 沥干, 在空气流或氧含量不大于 21% 的氮氧混合气中于 $150 \sim 700^\circ\text{C}$ 、优选 $200 \sim 500^\circ\text{C}$ 的温度范

围内保持 0.5 分钟~120 分钟, 优选 1 分钟~60 分钟, 以进行热分解。也可用氧化银代替硝酸银, 草酸银也可不析滤, 直接与有机胺络合, 然后浸渍载体。本发明的浸渍过程中使用的银化合物的量应足以使最后制备的催化剂中含银 1-30%重量, 优选 5~25%重量, 以催化剂总重量计。

本发明中的碱金属助剂可以是锂、钠、钾、铷或铯的化合物或其任意两种的组合, 例如锂、钠、钾、铷或铯的氧化物、氢氧化物、盐酸盐、硫酸盐、硝酸盐、碳酸盐、磷酸盐等, 优选铯的氧化物、氢氧化物、盐酸盐、硫酸盐、硝酸盐、碳酸盐、磷酸盐等, 更优选硫酸铯和碳酸铯。在最终的银催化剂中, 碱金属的含量基于最终催化剂重量为 5~2000ppm, 优选 10~1200ppm。碱金属助剂可在浸渍银之前、同时或之后施加到载体上, 也可以在浸渍过的载体活化以后浸渍在载体上。

本发明中的碱土金属助剂可以是镁、钙、锶或钡的化合物, 如氧化物、草酸盐、硫酸盐、醋酸盐或硝酸盐, 或其混合物, 优选醋酸盐, 更优选醋酸锶或醋酸钡。在最终的银催化剂中, 碱土金属的含量基于最终催化剂重量为 0~22000ppm, 优选 0~10000ppm。碱土金属助剂可在浸渍银之前、同时或之后施加到载体上, 也可以在浸渍过的载体活化以后浸渍在载体上。

本发明中的铈助剂可以是铈的氧化物、草酸盐、硫酸盐、醋酸盐或硝酸盐, 或其混合物, 优选铈的草酸盐和醋酸盐, 例如醋酸铈和草酸铈。在最终的银催化剂中, 铈的含量基于最终催化剂重量为 1~495ppm, 优选 5~200ppm。铈金属助剂可在浸渍银之前、同时或之后施加到载体上, 也可以在浸渍过的载体活化以后浸渍在载体上。

本发明中的铼助剂可以是铼的氧化物、高铼酸、高铼酸盐, 或其混合物, 优选高铼酸和高铼酸盐, 例如高铼酸、高铼酸铯和高铼酸铵。在最终的银催化剂中, 铼的含量基于最终催化剂重量为 0~1000ppm, 优选 0~400ppm。铼助剂可在浸渍银之前、同时或之后施加到载体上, 也可以在浸渍过的载体活化以后浸渍在载体上。

本发明中的铼助剂的共助剂可以是元素周期表中任一过渡金属的化合物, 或几种过渡金属化合物的混合物, 优选 VIB 族和 VIIB 族元素的

含氧酸及其盐，例如钨酸、钨酸铈、钼酸、钼酸铵。在最终的银催化剂中，铈助剂的共助剂的含量基于最终催化剂重量为 0 ~ 500ppm，优选 0 ~ 300ppm。铈助剂的共助剂可在浸渍银之前、同时或之后施加到载体上，也可以在浸渍过的载体活化以后浸渍在载体上。

催化剂性能的测定

本发明的各种银催化剂用实验室反应器(以下简称“微反”)评价装置测试其初始性能和稳定性。微反评价装置使用的反应器是内径为 4mm 的不锈钢管，反应器置于加热套中。催化剂的装填体积为 1ml，下部有惰性填料，使催化剂床层位于加热套的恒温区。

初始活性、选择性的测定

本发明使用的活性和选择性的测定条件如下：

反应气体组成(mol%)

乙烯(C ₂ H ₄)	28±1
氧(O ₂)	7.4±0.2
二氧化碳(CO ₂)	< 8
致稳气(N ₂)	余量
抑制剂二氯乙烷	0.1ppm-2.0ppm
反应压力	2.1MPa
空速	7000/h
反应器出口 EO 浓度	1.35%
时空产率	185 gEO/mlCat./h

当反应达到稳定后连续测定反应器入、出口气体组成。测定结果进行体积收缩校正后按以下公式计算选择性：

$$\text{选择性 } S = \frac{\Delta \text{EO}}{\Delta \text{EO} + 0.5 * \Delta \text{CO}_2} \times 100\%$$

其中 ΔEO 是出口气与进口气环氧乙烷浓度差， ΔCO_2 是出口气与进口气二氧化碳浓度差，取 10 组以上试验数据的平均数作为试验结果。

本发明和现有技术相比有如下优点：按照本发明制造的银催化剂使用多孔氧化铝载体，加入较少量的铈金属助剂，制备出具有较高的活性和选择性的银催化剂，这种催化剂特别适用于乙烯氧化生产环氧乙烷的

反应。

实施例

本发明下面结合实施例作进一步说明，但本发明的范围并不局限于这些实施例。

载体 1 和 2:

将 30 ~ 500 目的三水 α - Al_2O_3 312g, 30 ~ 200 目的假一水 Al_2O_3 104g, 石油焦 81g, NH_4F 7g, $\text{Mg}(\text{NO}_3)_2$ 8.5g 和 BaSO_4 分别为 0g、1.2g 放入混料器中混合均匀，转入捏合机中，加入稀硝酸(硝酸: 水=1: 3, 重量比)0.18 升，捏合成可挤出成型的膏状物。挤出成型为外径 8.0mm、长 6.0mm、内径 2.0mm 的环状物，在 80 ~ 120°C 下烘干 2 小时以上，使游离含水量降低到 10% 以下。

将上述 2 个环状物放入钟罩窑中，经 30 小时左右从室温升高到 1350°C ~ 1550°C 之间，恒温 2 小时，得到白色 α - Al_2O_3 载体样品 1 和载体样品 2。

载体 3:

将 30 ~ 500 目的三水 α - Al_2O_3 312g, 30 ~ 200 目的假一水 Al_2O_3 104g, NH_4F 7g, $\text{Mg}(\text{NO}_3)_2$ 8.5g 放入混料器中混合均匀，转入捏合机中，加入稀硝酸(硝酸: 水=1: 3, 重量比)0.15 升，捏合成可挤出成型的膏状物。挤出成型为外径 8.0mm、长 6.0mm、内径 2.0mm 的环状物，在 80 ~ 120°C 下烘干 2 小时以上，使游离含水量降低到 10% 以下。

将上述环状物放入钟罩窑中，经 30 小时左右从室温升高到 1350°C ~ 1550°C 之间，恒温 2 小时，得到白色 α - Al_2O_3 载体样品 3。

经测定，所得载体的组成和物性数据见表 1。

表 1 载体 1 ~ 3 的物性数据

	载体 1	载体 2	载体 3
α -氧化铝含量(%)	98.2	97.8	98.4
氧化钡含量(%)	0	0.35	0
压碎强度(N/粒)	52	47	86
吸水率(%)	61	64	47

堆比重(克/厘米 ³)	0.54	0.52	0.64
比表面(米 ² /克)	0.87	0.98	0.91
孔容(毫升/克)	0.68	0.65	0.58
孔半径分布(占总孔容%)			
<0.5 微米	20.5	19.8	17.0
0.5 ~ 1 微米	4.1	4.9	4.5
1 ~ 5 微米	51.4	53.5	63.7
5 ~ 10 微米	10.7	9.8	9.6
10 ~ 30 微米	9.2	9.6	3.4
30 ~ 51 微米	1.5	1.5	0.9
>51 微米	1.6	0.9	0.9

催化剂的制备:

比较例 1-3:

取 700g 硝酸银溶于 750ml 去离子水中, 得到硝酸银溶液。取 325g 草酸铵溶于 250ml 50°C 的去离子水中, 得到草酸铵溶液。在剧烈搅拌下混合这两种溶液, 生成白色草酸银沉淀。陈化 30 分钟以上, 过滤, 用去离子水洗涤沉淀至无硝酸根离子。滤饼含银约 60%, 含水约 15%, 为膏状物。

在带搅拌的玻璃容器中加入 300g 乙二胺, 110g 乙醇胺, 375g 去离子水。搅拌下把上面制得的草酸银膏状物慢慢加入混合液中, 温度保持在 40°C 以下, 使草酸银全部溶解, 草酸银的加入量使制得的浸渍液含银 22%(重量)。加 2.2g 硫酸铯、1.1g 醋酸钡, 再加去离子水使溶液总质量达到 2000g, 制成溶液待用。

分别取 100g 上面制备的载体样品 1、2 和 3 放入能抽真空的容器中。抽真空至 10mmHg 以上, 放入以上浸渍液, 浸没载体, 保持 30 分钟。沥滤去多余的溶液。浸渍后的载体在 400°C 的空气流中加热 5 分钟, 冷却, 即制成环氧乙烷银催化剂比较例 1、比较例 2 和比较例 3。

实施例 1-9:

重复与比较例 1-3 相同的程序, 不同的是浸渍液另外含有如下表 2 所示量的硫酸铯。

表2 实施例1-9 催化剂样品制备过程中铈助剂的加入量

实施例号	载体编号	硫酸铈加入量(g)
实施例1	1	0.09
实施例2	1	0.17
实施例3	1	0.35
实施例4	2	0.09
实施例5	2	0.17
实施例6	2	0.35
实施例7	3	0.09
实施例8	3	0.17
实施例9	3	0.35

对制成的催化剂的银和助剂含量进行分析,结果列于下表3,其中含量以金属计。

使用微型反应器评价装置在所述工艺条件下测定催化剂样品的活性和选择性,试验结果列于下表3。

表3 实施例1-9 催化剂样品的试验结果

实施例号	银含量(%)	Cs的含量(ppm)	Ce的含量(ppm)	反应温度(°C)	EO(%)	选择性(%)
比较例1	16.5	639	0	226.5	1.36	83.1
实施例1	17.0	642	15	221.8	1.36	83.7
实施例2	16.8	638	41	220.5	1.35	83.9
实施例3	17.1	635	103	223.6	1.37	83.6
比较例2	16.9	642	0	224.8	1.35	83.3
实施例4	17.2	645	16	221.0	1.36	83.9
实施例5	16.6	634	43	220.4	1.36	84.3
实施例6	17.1	640	112	222.0	1.34	83.7
比较例3	14.6	554	0	220.7	1.35	82.9
实施例7	17.2	668	11	217.4	1.38	83.5
实施例8	17.2	666	36	215.6	1.36	83.7
实施例9	17.3	662	87	216.8	1.35	83.6

比较例4

在带搅拌的玻璃容器中加入 300g 乙二胺, 110g 乙醇胺, 375g 去离子

水。搅拌下把如比较例 1-3 所述制得的草酸银膏状物慢慢加入混合液中，温度保持在 40°C 以下，使草酸银全部溶解，草酸银的加入量使制得的浸渍液含银 22%(重量)。加 2.2g 硫酸铯、2.3g 醋酸铯，再加去离子水使溶液总质量达到 2000g，制成溶液待用。

取 100g 上面制备的载体样品 2 放入能抽真空的容器中。抽真空至 10mmHg 以上，放入以上浸渍液，浸没载体，保持 30 分钟。沥滤去多余的溶液。浸渍后的载体在 300°C 的空气流中加热 5 分钟，冷却，即制成环氧乙烷银催化剂比较例 4。

实施例 10-12

重复与比较例 4 相同的程序，不同的是浸渍液另外含有如下表 4 所示量的醋酸铯或草酸铯。

表 4 实施例 10-12 催化剂样品制备过程中铯助剂的加入量

实施例号	铯助剂种类	加入量(g)
实施例 10	醋酸铯	0.19
实施例 11	醋酸铯	0.38
实施例 12	草酸铯	0.15

对制成的催化剂的银和助剂含量进行分析，结果列于下表 5，其中含量以金属计。

使用微型反应器评价装置在所述工艺条件下测定催化剂样品的活性和选择性，试验结果列于下表 5。

表 5 实施例 10-12 催化剂样品的试验结果

实施例号	银含量(%)	Cs 的含量(ppm)	Ce 的含量(ppm)	反应温度(°C)	EO (%)	选择性 (%)
比较例 4	16.5	639	0	224.7	1.36	83.3
实施例 10	17.0	642	43	220.8	1.36	83.7
实施例 11	16.8	638	98	219.3	1.35	84.3
实施例 12	17.1	635	47	221.6	1.37	83.8

比较例 5

在带搅拌的玻璃容器中加入 300g 乙二胺，110g 乙醇胺，375g 去离子水。搅拌下把如比较例 1-3 所述制得的草酸银膏状物慢慢加入混合液中，

温度保持在 40°C 以下,使草酸银全部溶解,草酸银的加入量使制得的浸渍液含银 22%(重量)。加 2.2g 硫酸铯,再加去离子水使溶液总质量达到 2000g,制成溶液待用。

取 100g 上面制备的载体样品 2 放入能抽真空的容器中。抽真空至 10mmHg 以上,放入以上浸渍液,浸没载体,保持 30 分钟。沥滤去多余的溶液。浸渍后的载体在 300°C 的空气流中加热 5 分钟,冷却,即制成环氧乙烷银催化剂比较例 5。

实施例 13-14

重复与比较例 5 相同的程序,不同的是浸渍液另外含有 0.35g 和 3.8g 硫酸铯。

对制成的催化剂的银和助剂含量进行分析,结果列于下表 6,其中含量以金属计。

使用微型反应器评价装置在前述工艺条件下测定催化剂样品的活性和选择性,试验结果列于下表 6。

比较例 6

重复与比较例 5 相同的程序,不同的是浸渍液另外含有 5.0g 所示量的硫酸铯。

对制成的催化剂的银和助剂含量进行分析,结果列于下表 6,其中含量以金属计。

使用微型反应器评价装置在前述工艺条件下测定催化剂样品的活性和选择性,试验结果列于下表 6。

表 6 实施例 13 催化剂样品的试验结果

实施例号	银含量(%)	Cs 的含量(ppm)	Ce 的含量(ppm)	反应温度(°C)	EO (%)	选择性 (%)
比较例 5	16.5	639	0	223.7	1.36	82.7
实施例 13	17.0	642	43	217.3	1.34	83.5
实施例 14	16.8	633	452	221.9	1.35	83.0
比较例 6	16.1	612	623	227.0	1.35	82.6

比较例 7

在带搅拌的玻璃容器中加 300g 乙二胺, 110g 乙醇胺, 375g 去离子水。搅拌下把如比较例 1-3 所述制得的草酸银膏状物慢慢加入混合液中, 温度保持在 40°C 以下, 使草酸银全部溶解, 草酸银的加入量使制得的浸渍液含银 22%(重量)。加 2.0g 硫酸铯、0.6g 高铼酸和 0.1g 钼酸铵, 再加去离子水使溶液总质量达到 2000g, 制成溶液待用。

取 100g 上面制备的载体样品 2 放入能抽真空的容器中。抽真空至 10mmHg 以上, 放入以上浸渍液, 浸没载体, 保持 30 分钟。沥滤去多余的溶液。浸渍后的载体在 230°C 的空气流中加热 5 分钟, 冷却, 即制成环氧乙烷银催化剂比较例 7。

实施例 15

重复与比较例 5 相同的程序, 不同的是浸渍液另外含有 0.35g 所示量的硫酸铯。

对制成的催化剂的银和助剂含量进行分析, 结果列于下表 6, 其中含量以金属计。

使用微型反应器评价装置在所述工艺条件下测定催化剂样品的活性和选择性, 试验结果列于下表 6。

表 6 实施例 15 催化剂样品的试验结果

实施例号	银含量 (%)	Cs 的含量 (ppm)	Ce 的含量 (ppm)	Re 的含量 (ppm)	Mo 的含量 (ppm)	反应温度 (°C)	EO (%)	选择性 (%)
比较例 7	16.5	639	0	205	32	227.4	1.36	83.9
实施例 15	17.0	642	43	210	35	222.6	1.34	84.7